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ELECTRONIC ABSORPTION SPECTRA OF INORGANIC AND ORGANIC COMPOUNDS OF NITROGEN: I. NITROGEN DIOXIDE-DINITROGEN TETROXIDE IN SOLUTION

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Abstract

The electronic absorption spectra for NO_2-N_2O_4 mixtures has been measured in various non-polar and polar solvents. In non-polar solvents the spectra is very similar to NO_2-N_2O_4 mixtures in the gas state. However, in solvents with unshared electron pairs available particularly ethers, esters, ketones and tertiary amines, a complex multi-banded spectra is observed at room temperature. This spectra appears to be characteristic of NO_2 - N_2O_4 in those solvents and to be the result of the same electron donor-acceptor type molecular complexes reported previously in the literature at lower temperatures in the solid state. In olefins and n-alkyl amines reactions occur and the products formed are discussed.

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Despite the general interest in the physical and chemical properties of NO_2 - N_2O_4 mixtures, both from the fundamental standpoint and in applied research on air pollution and rocket propulsion, there has been relatively little work on the ultraviolet absorption spectra of NO_2 - N_2O_4 mixtures below 2400 Å in the gas state[2,3] and only a few incidental spectra for NO_2 - N_2O_4 in solution.[4,5] However, a considerable

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(1) Presented in part at the 132nd meeting of the American Chemical Society, New York City, New York, September 1957.

(2) T. C. Hall, Jr. and F. E. Blacet, J. Chem. Phys. 20, 1745 (1952).

(3) Harris, King, Benedict and Pearse, J. Chem. Phys. 8, 765 (1940).

(4) C. C. Addison and C. P. Conduit, J. Chem. Soc. 1952, 1390.

(5) J. V. L. Longstaff and K. Singer, J. Chem. Soc. 1954, 2604.

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amount of research has been done on molecular complexes between nitrogen oxides and ethers, ketones, acids, esters, nitrites, and amines.[6-17] Most

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(6) P. Gray and A. D. Jaffe, Chem. Revs. 55, 1069 (1955).

(7) B. Rubin, H. H. Sisler and H. Schechter, J. Amer. Chem. Soc. 74, 877 (1952).

(8) J. G. Whanger and H. H. Sisler, Ibid., 75, 5188 (1953).

(9) H. W. Ling and H. H. Sisler, Ibid., 75, 5191 (1953).

(10) D. A. Davenport, H. J. Buckhardt and H. H. Sisler, Ibid., 75, 4175 (1953).

(11) B. J. Gibbons, G. L. Eichhorn and H. H. Sisler, Ibid., 76, 4668 (1954).

(12) H. H. Sisler and P. E. Perkins, Ibid., 78, 1135 (1956).

(13) C. C. Addison, C. P. Conduit and R. Thompson, J. Chem. Soc., 1952, 1303.

(14) C. C. Addison, N. Hodge and J. C. Sheldon, Chemistry and Industry, 1953, 1338.

(15) C. C. Addison and J. Lewis, Quart. Revs. (London) 9, 115 (1955).

(16) A. E. Comyns, Nature, 172, 491 (1953).

(17) A. E. Comyns, J. Chem. Soc., 1955, 1557.

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of this work has involved cryoscopic investigations of these complexes at low temperatures; however, some application of viscosimetry and of infrared and Raman spectroscopy[7] has been made.

It was of interest to obtain ultraviolet spectra of $NO_2 - N_2O_4$ in a number of solvent systems. The results obtained indicate the presence of molecular complexes of nitrogen oxide with electron donor type solvents in dilute solution.

EXPERIMENTAL DETAILS

The nitrogen dioxide ($NO_2 - N_2O_4$) was added to the solvents from a Matheson lecture cylinder. The gas was dried by passage through a P_2O_5 filled U tube before entering the solvents.

The solvents used were of spectroscopic purity or of reagent grade. Most of these solvents were further treated by two different methods to remove traces of water and alcohol. In one set of spectroscopic measurements, the solvents were passed through alumina

columns to remove peroxides and some residue aldehyde and then they were passed through molecular sieve material to remove water and some alcoholic impurity. In the second set of measurements, the solvents were dried over the appropriate solid drying agent[18] with frequent

(18) A. Weissberger, et. al., Techniques in Organic Chemistry, Vol. VII. Organic Solvents. Interscience Publishers, New York, 1955.

agitation followed by distillation. The ethers used were tested for peroxides by the KI method.[18] The spectroscopic grades of cyclohexane and isooctane from Phillips Petroleum were used as received. In several determinations NO_2 - N_2O_4 was added to diethyl ether obtained from a container of Mallinckrodt anhydrous reagent grade diethyl ether (< 0.01% alcohol, < 0.01% water) opened immediately before the spectroscopic measurement.

The spectroscopic work was done using a Cary Model 11 Recording Spectrophotometer at room temperature. The details of the instrumental operation and the accuracy and reproducibility of results are discussed elsewhere.[19]

(19) A. P. Altshuller, I. Cohen, and C. M. Schwab, J. Phys. Chem. (1958).

Measurements below 2200 A were done using 1 mm. absorption cells. Owing to the excellence of the double monochromator, stray light is negligible at 2100 A and above, transmittance of stray light is about 0.5% at 2050 A and about 3.5% at 2000 A. The three solvents used for detecting the absorption bands below 2200 A were Phillips spectroscopic grade cyclohexane and isooctane and Mallinckrodt anhydrous reagent grade diethyl ether. The cyclohexane, compared with distilled water, showed 80%

transmission at 2200 A, 75% at 2100 A, 70% at 2050 A, while the isooctane showed 90% transmission at 2200 A, 65% at 2100 A and 50% at 2050 A. The Mallinckrodt diethyl ether showed about 85% transmission at 2200 A, 40% at 2100 A and 10% at 2050 A, compared to distilled water.

RESULTS AND DISCUSSION

The ultraviolet absorption spectra of nitrogen dioxide-dinitrogen tetroxide have been determined in cyclohexane, 2,2,4-trimethylpentane (isooctane), 2,4,4-trimethylpentene-1, carbon tetrachloride, chlorobenzene, diethyl ether, di-i-propyl ether, dioxane, ethyl acetate, acetone, n-butyl amine, pyridine and water. The absorption maxima are listed in Table I.

In the gas state the spectra of NO_2 and N_2O_4 have been separated by making measurements at various pressures.[2,3] The results for gaseous nitrogen dioxide show relatively little absorption above 5000 A, a broad fine structured absorption band from 5000 A down to about 3000 A with a maximum around 4000 A, and decreasing absorption to 2500 A.[2] From 2500 A down to about 2300 A there are some fine structured bands which are no more than about one-third as strong as the broad band in the 3000 to 5000 A region.[1,2] No data appear to be available below 2300 A so it is not established just where the next strong absorption band for NO_2 would occur. In contrast, N_2O_4 shows no absorption above 4000 A, a broad structureless band between 3000 A and 4000 A with a maximum at 3400 A, a minimum at 3050 A, and increasing absorption to 2400 A and below.[2] A shoulder appears at about 2600 A on the stronger absorption band, which has a maximum somewhere below 2400 A.[2]

In the present investigation it was found that for the NO_2 - N_2O_4

mixture in the nonpolar solvents -- hexane, cyclohexane, isooctane and carbon tetrachloride -- as well as in the polar solvent -- chlorobenzene -- a broad peak is observed very near 3400 A, a minimum between 3000 and 3100 A and increasing absorption towards the short wavelength limit. Absorption between 4000 and 6000 A was present owing to the NO_2 in equilibrium with the N_2O_4. The total concentration of NO_2 - N_2O_4 added was in the 0.1% or 1000 part per million range. In this concentration range in the gaseous state very little N_2O_4 would be present; however, in halogenated organic solvents and in hydrocarbons the amount of N_2O_4 in equilibrium with NO_2 is very appreciable.[6] The NO_2 vibrational fine structure was observable in considerable detail in the hydrocarbons used. In carbon tetrachloride the fine structure of NO_2 is still observable but much of the detail has disappeared, while in chlorobenzene no fine structure can be distinguished.

Absorption peaks for NO_2 - N_2O_4 in isooctane and cyclohexane are observed at or below 2050 A. One might conclude from the gas phase spectra that these peaks are assignable to the N_2O_4 molecule. However, the lack of data on the gas spectra of NO_2 - N_2O_4 in this region makes a definite assignment hazardous. It is possible that the absorption in solution is actually near or below 2000 A, since these measurements press the limit of the instrument used. While agreement was obtained with the literature when the short wavelength peak of benzene in hydrocarbons was measured, the absorption bands for nitrate and bromide ions and for hexene-1 were observed slightly above 2000 A instead of below 2000 A as reported in the vacuum ultraviolet literature.

The spectra of $NO_2 - N_2O_4$ in n-butyl amine also showed a single broad peak in the 3000 to 4000 A region, but the peak is displaced to 3770 A. This peak can be associated with the nitrosation of the primary amine to give butyl nitrosamine.[6,20] Fuming was very pronounced upon addition of the $NO_2 - N_2O_4$ to the butyl amine and a large amount of

(20) R. N. Haszeldine and B. J. H. Mattinson, J. Chem. Soc. 1955, 4172.

deamination of the butyl amine to butyl alcohol and nitrogen certainly must occur also.[6]

The absorption spectra of the $NO_2 - N_2O_4$ mixture in 2,4,4-trimethylpentene-1 can be anticipated to represent a complex reaction product consisting of a mixture of organic nitrogen oxide compounds.[6] The band at 6700 A which gives the solution a greenish-blue coloration can be assigned to an aliphatic nitroso group[21] while the band system in the 3000 to 4000 A region is similar to that of an n-alkyl or i-alkyl

(21) J. Jander and R. N. Haszeldine, J. Chem. Soc. 1954, 912.

nitrite. If one of the reaction products is a compound with a - N = O group attached to the 2-carbon and a - O - N = O group attached to the 1-carbon just such a spectrum would be obtained. In one determination the spectrum in the 3000 to 4000 A region resembled that of a t-alkyl nitrite. In such a case the O - N = O group would be attached to the 2-carbon atom. Such a compound, in dimeric form, was postulated some years ago as a result of a chemical study of the reaction products of $NO_2 - N_2O_4$ with 2-methylpropane.[22] The presence of nitroalkanes and

alkyl nitrates cannot be shown by ultraviolet spectroscopy, but these compounds should be identifiable by their infrared spectra.[23]

(22) A. Michael and G. H. Carlson, J. Org. Chem. 5, 1-13 (1940).

(23) J. F. Brown, Jr., J. Amer. Chem. Soc. 77, 6341 (1955).

When the nitrogen oxides are added to the oxygenated solvents, diethyl ether, di-i-propyl ether, dioxane, ethyl acetate and acetone, and to the tertiary amine, pyridine, a multi-banded spectrum is observable in the 3000 to 4000 A region. Above 4000 A the ethyl acetate and acetone showed no absorption; however, nitrogen oxide in diethyl ether did show a slight tail absorption extending well into the visible region.

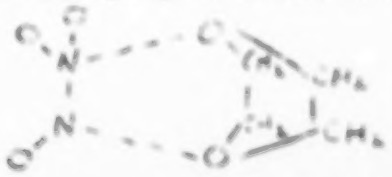
Nitrous acid and alkyl nitrites also have multi-banded spectra in the 3000 to 4000 A region. Considerable care was taken to treat the solvents used so as to remove traces of water which could react with the nitrogen oxides to form nitrous acid, and to remove alcohol, primarily traces of methanol and ethanol, which could react with the nitrogen oxides to form methyl and ethyl nitrite. The many-band spectrum persists despite the two different treatments used to remove water and alcohol. Furthermore, the positions of the peak maxima for the NO_2 - N_2O_4 in oxygenated solvents and in pyridine is displaced upwards by as much as 50 to 60 A compared to the peak positions of alkyl nitrites or nitrous acid. Also, there is a quite sharp band at 3880 to 3900 A in the NO_2 - N_2O_4 systems which is not present in methyl nitrite, ethyl nitrite, nitrous acid or in the nitrogen oxides in water.

Further evidence for the existence of a unique spectrum for

$NO_2 - N_2O_4$ mixtures in oxygenated solvents and tertiary amines is given by the strong peak maxima observed below 2400 A. It is possible to locate a peak at about 2050 A for $NO_2 - N_2O_4$ in diethyl ether. However, the band maximum observed for alkyl nitrites in ethyl ether are above 2200 A. On the other hand, the band maximum for nitrite ion in distilled water is at 2110 A, and the band maximum for nitrite in water at a pH of 2, in which it exists largely as nitrous acid is also at 2110 A. Consequently, the peak at 2050 A is also characteristic of $NO_2 - N_2O_4$ in diethyl ether.

Since isolatable molecular complexes between nitrogen oxides and ethers, esters, ketones, acids, nitrites and tertiary amines are well established as existing in many cases below 0° and, in at least one instance, the nitrogen oxide-dioxane complex, to 45°,[6-17] it seems most likely that the observed ultraviolet spectra at room temperature for $NO_2 - N_2O_4$ in ethers, acetone, ethyl acetate and pyridine are the result of similar complexes existing in solution. The large excesses of solvent present would repress dissociation of the complexes in the dilute solutions prepared, i.e., approximately 0.1% nitrogen oxides. Consequently, it is possible to use ultraviolet spectroscopy to follow the variations in such complexes of nitrogen oxides with electron donor solvents as a function of composition and temperature.

The exact nature of these complexes has not yet been resolved. Sisler and co-workers contend that the complexes involve N_2O_4 complexing with the electron donor groups in ethers in the following manner:[7]



Addison and his co-workers[13-15] believe that their data indicate complexes of tertiary amines with the nitrogen oxide of the form

$$B \longrightarrow :\ddot{N} - O:^{+} \longrightarrow \underset{B}{:\dot{N}} - O:^{+}$$

No evidence has been found of ionic species involving NO^{+} from either magnetic susceptibility measurement nor Raman spectra for nitrogen oxide-ether complexes.[7]

It seems quite possible that different types of complexes may form between nitrogen oxide and oxygenated compounds and nitrogen oxide and tertiary amines. While the individual peaks in the 3000 to 4000 Å region for nitrogen oxide in pyridine are very slightly higher than for nitrogen oxide in the oxygenated solvents, the spectra of the two solutions above 3000 Å certainly are not sufficiently different to provide evidence for a difference in the structure of the complexes. Indeed, the view has been expressed previously in the literature that molecular compounds are formed between N_2O_4 and ethers, nitriles and even heterocyclic amines, but that the tertiary aliphatic amines which are very strong donors, form ionic complexes.[24] A study of the magnetic susceptibility, infrared

(24) C. C. Addison and J. C. Sheldon, J. Chem. Soc., 1941 (1956).

and Raman spectra of the nitrogen oxide-tertiary amine complexes and especially an X-ray diffraction investigation of the molecular structure of these complexes should lead to a clarification of the detailed nature of these compounds.

ANALYTICAL IMPLICATIONS

The study of the ultraviolet spectra of NO_2 - N_2O_4 in various

solvent systems along with ultraviolet investigations of organic nitrogen oxide-like compounds[19] provides spectral information of analytical significance.

The absorption band for NO_2 - N_2O_4 in the molecular complexes at 3880 to 3900 A can be used to distinguish NO_2 - N_2O_4 from alkyl nitrites in solution. Owing to the relative weakness of the band and the background absorption this peak can only be used for qualitative and semi-quantitative purposes. It is estimated from some work with alkyl nitrite NO_2 - N_2O_4 mixtures that a minimum of 10 to 20% of NO_2 - N_2O_4 would have to be present relative to the alkyl nitrite to detect the presence of the nitrogen oxide.

It is possible also to use the fine structured band of NO_2 above 4000 A observed in hydrocarbons and carbon tetrachloride to detect and analyze for NO_2 in the presence of alkyl nitrites, alkyl nitrates or nitroalkanes. Since the band system for NO_2 in the visible is weak, concentration to about 0.1% is necessary.

The peroxyacetyl nitrite identified in nitrogen oxide-olefin mixtures subject to photolysis in the laboratory and in the atmosphere,[25,26]

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(25) E. R. Stephens, et. al., Proc. API 36 [III] 288 (1956).

(26) W. E. Scott, et. al., paper presented at 22nd midyear meeting of API Division of Refining, Philadelphia, Pennsylvania, May 14, 1957.

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shows a very weak absorption in the 3000 to 5000 A region compared with ethyl nitrite.[26] Consequently, nitrogen dioxide-dinitrogen tetroxide mixtures can be identified in the presence of the peroxy acetyl nitrite by either NO_2 - N_2O_4 absorption peaks in the 3000 to 4000 A region or

by the fine structured nitrogen dioxide absorption between 4000 and 5000 A. In either region it again would be necessary to concentrate to the 1000 ppm range. Unfortunately, the peroxyacetyl nitrite band in the 2000 to 3000 A range has not yet been reported.

In the region below 2300 A, one finds the alkyl nitrites have absorption peaks between about 2100 in water to 2200 - 2240 A in slightly polar organic substances and hydrocarbons.[19] The nitrite ion in aqueous solution has a peak at 2110 A. It has been found in measurements we have made on ethyl through amyl nitrates in hydrocarbons, methanol and water that the absorption peaks are at or below 2050 A. Similarly, nitroethane in hydrocarbons has a peak below 2050 A. Both the nitrate ion and nitrogen dioxide in solution also have peaks below 2050 A. Consequently, the alkyl nitrites are easily distinguished from these other inorganic and inorganic nitrogen oxide-like compounds in the 0.01 to 0.001 weight percent range. Unfortunately, owing to the broadness of the alkyl nitrite band, it is only possible in mixtures of different classes of nitrogen compounds to resolve partially the band resulting from the alkyl nitrite from those resulting from these other classes of nitrogen compounds.

Acknowledgement: The authors wish to thank Israel Cohen for assistance in obtaining some of the ultraviolet spectra during the course of this investigation.

Table I. Ultraviolet Absorption Spectra of Nitrogen Dioxide in Various Solvents

Solvent	Wavelength, A							
	A	B	C	D	E	F	G	H
Cyclohexane			broad peak, maximum at 3430					<2050
Isooctane			broad peak, maximum at 3420					<2050
2,4,4-trimethylpentene-1[a]		3810	3680	3550	3425	-	-	-
Carbon Tetrachloride			broad peak, maximum at 3430					-
Chlorobenzene			broad peak, maximum at 3400					-
Diethyl Ether	3900	3740	3605	3480	3375	3280	-	<2050
Di-i-propyl Ether	3900	3745	3610	3490	3380	3275	3200	
Dioxane	3890	3730	3600	3475	3365	3260	-	-
Ethyl Acetate	3880	3730	3590	3470	3360	3245	-	-
Acetone	3890	3740	3600	3480	3380	3280	-	-
n-Butyl Amine			broad peak, maximum at 3770					-
Pyridine	3910	3750	3620	3500	3395	3295	-	-
Water	3850	3710	3580	3460	-	-	-	<2100

[a]Peak at 6700 A